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NASA

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ABSTRACT: Optical and scanning electron microscopy were used to investigate the failure morphology of $(0°)_8$ T300/5208 graphite/epoxy specimens which had been tested until tensile failure. Failure morphology was studied as a function of the quality control variables of specimen preparation technique, prepreg batch, and cure condition, and also as a function of the environmental parameters of temperature and moisture content. Defective specimens were found to exhibit a low-energy failure morphology. Poor specimen edge preparation and one batch of prepreg — when tested at elevated temperature or moisture content — also exhibited this low-energy failure morphology. Postcuring had no effect on strength but did slightly alter failure morphology. Temperature or moisture appeared to decrease flaw sensitivity and thus increase strength; however, moisture also appeared to increase interfacial debonding between filament and matrix. When combined moisture and temperature increased interfacial debonding and made the epoxy matrix more prone to fracture.

KEY WORDS: Composite materials, graphite/epoxy composites, failure morphology, scanning electron microscopy, environments, moisture

While high performance composite materials have enormous potential for use in advanced aircraft structures, such utilization is hindered by the current inability to ensure structural reliability comparable to that of existing metal components. Because of the unique properties of composites, new predictive methodologies based on an understanding of the underlying mechanisms that

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control properties must be developed. This approach will ensure that the results of short-term accelerated testing will yield predictions applicable to long-term behavior. The work reported here is a portion of a NASA-Ames Research Center study investigating the effects of potential accelerating parameters on the mechanisms of failure of state-of-the-art graphite/epoxy composites. The study is a follow-up to the earlier work of Clements and Lee [1], who investigated the influence of several "quality control" and environmental variables on the tensile properties of $(0°)_8$ Thornel 300/5208 graphite/epoxy composites. In the current work, optical and scanning electron microscopy were used to investigate the failure surfaces of the graphite/epoxy composite specimens tested by Clements and Lee, with the aim of correlating the failure morphologies with the observed tensile strengths.

Experimental Procedure

Materials and Specimen Fabrication

The "T300/5208" graphite/epoxy composite was fabricated from prepreg tape manufactured by NARMCO Materials, Inc., which was composed of Union Carbide Corporation's WYP-30-1/0 (3000 filament, zero twist) grade of Thornel 300 graphite fiber and NARMCO's 5208 epoxy resin. The properties of these materials are described in Ref. 1. The specimens used for the mechanical study were fabricated by an outside vendor; however, numerous specimen defects required extensive screening and rework of the specimens. Details of the specimen fabrication, screening, and rework are also given in Ref. 1. Briefly, during screening, specimens that showed obvious bow or other irreparable damage were rejected. The specimens were then reworked by wet-polishing the cut edges to remove all detectable (at 30X) torn or delaminated material. In addition, some of the specimens were screened for bow and for visually obvious edge defects but were not reworked by edge polishing. The results from these

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specimens were then compared with those from polished-edge specimens. The nominal configuration was 12.7 mm wide for specimens with unpolished edges, 10 to 12 mm wide for specimens with polished edges, by 1.2 mm thick, 127 mm gage length, and 60-mm-long fiberglass tabs.

Specimens from two prepreg batches were examined. Batch A specimens gave "normal" mechanical behavior, but specimens from prepreg batch B showed anomalous mechanical behavior in early tests. The differences between the two batches will be described more fully under Results and Discussion.

The effects of cure condition were also considered. Some of the specimens were tested as received (cured 1/2 h at 135°C and 2 h at 180°C), while others were postcured for 2 h at 200°C, followed by a slow oven cool.

Environmental Conditioning

Environmental conditioning is described in detail in Ref. 1. All specimens were dried in a vacuum desiccator (at 100°C for 7 days) before moisture conditioning. Specimens to be tested "dry" were then held in a room temperature vacuum dessicator until they were tested. "Wet" specimens were placed, after drying, in an environmental chamber at 60°C and approximately 100% relative humidity (r.h.) for at least 60 days and then were held at room temperature (~25°C) and approximately 100% r.h. for at least 45 days before testing. The resulting water content of the "wet" specimens was 2.02 ±0.13% (by weight).[3] The moisture condition of the specimens will be discussed further under Results and Discussion.

Mechanical Testing

Specimens were tested until failure at a tensile strain rate of $3 \times 10^{-5} \ \text{s}^{-1}$. Tests were performed inside an environmental chamber held at the desired temperature and at <5% r.h. for the dry specimens or ~100% for the wet specimens. The testing details and results of the mechanical study are given in Ref. 1.

Microscopy

After failure, the specimens were "reassembled" as much as possible and photographed to record the relative locations of failed regions. The failure surfaces were also examined visually and with a low-power optical microscope, and general observations of failure morphology were recorded. The failure regions were then mounted and sputter-coated with gold for scanning electron microscopy (SEM) examination. In addition, for some of the specimens, sections were taken from the tab regions or from unfailed regions and were mounted in epoxy, polished, and examined with an optical metallograph.

Experimental Matrix

The "quality-control" variables considered were:

Specimen preparation technique:	Polished edges (per ASTM 3039-76)
	Unpolished edges
Prepreg batch:	A — normal mechanical behavior
	B — anomalous mechanical behavior
Cure condition:	Not postcured (as received)
	Postcured 2 h at 200°C

The environmental variables studied were:

Temperature:	25° and 96°C
Moisture content:	Dry ≅ 0% (tested at <5% r.h.)
	Wet ≅ 2% (tested at ~100% r.h.)

In the previous study, Clements and Lee [1] mechanically tested four to eight specimens at nearly every combination of variables from this experimental matrix. However, in the case of specimens with unpolished edges, only specimens from batch A, mostly unpostcured, were tested. Table 1 summarizes the tensile strengths reported by Clements and Lee. For the current work, the

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results of the mechanical testing led us to select unpostcured batch A specimens with polished edges as our "standard" specimens. Nevertheless, we studied in some detail most of the conditions from the mechanical test matrix. First, we visually examined all of the mechanically tested specimens without magnification and with a low-power microscope. Then we proceeded to an SEM examination of selected specimens. Our initial SEM work revealed that there was considerable specimen-to-specimen and area-to-area variability in failure morphology. Thus, two or three unpostcured and one or two postcured specimens were examined for batches A and B specimens, with polished edges, at each environmental condition. Generally, five or more areas were examined in each specimen. Fewer numbers of specimens with unpolished edges and with known flaws were examined.

Results and Discussion

General Observations

SEM failure-surface examination revealed some general types of failure morphologies resulting from different types of failure propagation modes. Figure 1 illustrates the two most distinctive morphologies. The failure surface in Fig. 1a shows a varied topography with filaments and filament bundles at many different heights. The fracture path in this specimen was quite circuitous, and in fact was probably due not to a single crack but rather to a coalescence of cumulative damage. By analogy with metals, we assume that this morphology resulted from relatively "high energy" failure propagation. On the other hand, the failure surface in Fig. 1b is relatively smooth. As the higher magnification fiew in Fig. 1c shows, this smoother surface even displays the "river patterns" (striations perpendicular to the moving crack front — see arrow) — due to stopping and starting of a propagating crack — which are typical of more homogenous materials. This topography indicates that the failure crack

went through the material easily, with little secondary damage (such as intersecting secondary cracks) or other hindrance to its direct progress. We assume that this morphology results from relatively "low-energy" failure propagation.

Many specimens clearly failed by one or the other of these modes, but some specimens appeared to fail by a mixture of the two modes. Again, by analogy with metals, we assume that these specimens failed by "mixed-mode" failure propagation. Other specimens did not fail by these modes; however, in almost all of these specimens the failure mode was somehow suspect. These specimens included those that failed in or at the tabs, some that failed by splitting and delamination (which frequently was suspected to have originated in the tabs), and a number of batch B specimens which failed in an unusual manner which will be described in a later section.

A distinct relationship was found between the failure mode and the strength of the specimens. For example, all but one of the batch A specimens with polished edges that failed by low-energy failure propagation had strengths well below the mean value. Furthermore, low-energy failure propagation was the typical failure mode for "reject" specimens with known defects such as severe notches or bow; often, the origin of the failure path could be traced back directly to the defect. These observations led us to believe that in "good" specimens, low-energy failure propagation resulted from an undetected defect. Low-energy failure propagation, as an indicator of a defective specimen, becomes important in our analysis of the influence of quality control and environmental variables on failure, to be described in the following sections.

Influence of Specimen Preparation Technique

As was reported in Ref. 1, the strength of specimens having polished edges was found to be 15 to 25% higher than that of specimens with unpolished

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edges. Figure 2 compares a typical scanning electron micrograph of a polished edge (Fig. 2a) to one of an unpolished edge (Fig. 2b). While the polished edge has individual damaged filaments, the unpolished edge shows numerous areas where groups of filaments are damaged. An examination of specimen failure mode revealed the apparent effect of these groups of damaged filaments on the failure of unpolished-edge specimens. More than 60% of the specimens with unpolished edges failed by low-energy failure propagation, and the balance failed at the tabs or by splitting and delamination. On the other hand, more than 70% of the specimens with polished edges failed by high energy or mixed modes; few failed by low-energy failure propagation. We conclude that the damaged edges of the unpolished-edge specimens constituted defects which produced the low strengths observed.

Influence of Prepreg Batch

As was reported in Ref. 1, optical microscopy, SEM, and consultation with NARMCO and Union Carbide led us to conclude that the epoxy within and around some of the individual fiber bundles in the batch B prepreg had been altered and degraded. Presumably, this occurred because the epoxy reacted to a surface contaminant on some of the fiber tows (fiber bundles) used to make up the prepreg. Whatever the cause of the properties of batch B material, mechanical testing did show a distinct difference in the behavior of batch B versus the "normal" batch A material. At 25°C dry, the strength of the batch B material was statistically the same as that of batch A, but at 25°C wet and 96°C dry, batch B strengths were significantly lower than batch A. (As will be described later, we were unable to test to failure at 96°C wet.) This strength difference was paralleled by a difference in failure modes. At 25°C dry most of the batch B failures were mixed mode, but with a predominance of low-energy failure regions. At the same condition, most of the batch A specimens also failed by

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mixed mode, but high-energy regions predominated. At 25°C wet and 96°C dry, however, most of the batch B specimens failed by the low-energy mode, with the exception of some that failed at the tabs. Metallographic examination of these specimens revealed that almost all were split (in the 0° direction) underneath the end tabs. Also, Clements and Lee were unable to test the batch B specimens at 96°C wet because the specimens split and crushed underneath the tabs when the tensile grips were tightened before testing. In Ref. 1 this problem was attributed to bad end-tab adhesive, but after examination of the less severe splitting which occurred at 25°C wet and 96°C dry, we concluded that the splitting at 96°C wet was at least partially due to deterioration of the composite itself.

SEM examination of the failure surfaces of batch B specimens detected differences in the fiber bundles in the specimens. Figure 3 illustrates this difference in a low-energy failure region. Even in such a relatively smooth area individual fiber bundles stand out. In other specimens, the borders between fiber bundles were traced as the location of a 0° split in the composite, and in others a delamination seemed to originate at the border betwen such bundles. We conclude from these observations that the regions of altered epoxy associated with some of the batch B fiber bundles led to a different failure mode for batch B specimens and to lower strengths at elevated temperature or moisture content. At 25°C dry the differences in failure modes in batches A and B are only slight, thus the strength effect is minimal. (The batch B mean strength is lower than batch A, but the difference is not statistically significant.) The altered epoxy has a more important influence at elevated temperature or moisture content, however, and apparently produces severe degradation when temperature and moisture are combined.

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Influence of Cure Condition

The strength data of Clements and Lee [1] showed no effect of cure condition. Nevertheless, an analysis of failure morphology revealed some slight differences, on the average, between specimens which were not postcured and those which were. All conclusions stated above for quality control variables and later for environmental parameters hold for postcured specimens as well as those not postcured. However, failure surfaces of the postcured specimens on the average seem to have somewhat longer and cleaner filaments. In addition, the epoxy appears to be somewhat more brittle than in specimens which were not postcured. These differences, however, are slight, so the absence of a statistical influence on strength is as expected.

Influences of Temperature and Moisture Content

Clements and Lee reported that the longitudinal tensile strength of batch A specimens with polished edges increased significantly as temperature increased from 25° to 96°C. They also reported that an increase in moisture content from dry to wet produced no significant change in strength. However, our conclusion regarding low-energy failure propagation as indicative of a defective specimen has led us to reconsider these data. If we eliminate from statistics all specimens that failed by low-energy failure propagation, the batch A failure data are as shown in Table 2. Now we find a significant increase in longitudinal tensine strength with both increasing temperature and increasing moisture content. We believe that this latter conclusion reflects more accurately the actual material behavior of "normal" (batch A or equivalent) T300/5208 graphite/epoxy. (The reader should note, however, that such behavior as a function of temperature and moisture content is representative only of 0° laminates and should not be generalized to any other configuration.)

Figure 4 shows representative failure morphologies for unpostcured batch A specimens with polished edges at the four environmental conditions considered. It should be noted that while a representative micrograph is given for 96°C wet, early end-tab failures on many of the specimens cast doubt upon all of the strength data at this condition. Thus, Clements and Lee did not report 96°C wet strength in Ref. 1. (The data we show in Tables 1 and 2 are taken from their raw data.)

In examining Fig. 4, it is also important to remember that there was considerable specimen-to-specimen and area-to-area variation in morphology for all conditions. Thus, these micrographs in no way represent the diversity of morphologies encountered at any environmental condition, but rather are typical of the most common or average morphology at that condition.

The influence of temperature on failure can be explored by comparing the behavior at 25°C dry and 96°C dry. We found that the differences in failure morphology for these two conditions were again related to failure mode. At 25°C dry there were no failures which were uniquely high-energy mode — most were mixed mode. That is, even though the high-energy mode might predominate in a specimen, there were occasional low-energy regions. At 96°C dry, on the other hand, there were no mixed-mode failures. Most specimens failed by the high-energy mode, although there were a few (presumably defective) specimens which failed by the low-energy mode. Furthermore, at 96°C dry the failure surfaces were macroscopically more irregular. That is they had a more varied topography, possibly resulting from more secondary damage and thus a higher energy failure at 96°C than at 25°C. We hypothesize that these differences may be due to a decrease in flaw sensitivity with increased temperature.

A comparison of failure morphologies at 25°C dry and 25°C wet illustrates the influence of moisture on failure. At 25°C wet a few specimens showed

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mixed-mode failures, but most clearly failed by either the high- or the low-energy modes. The failure surfaces at 25°C wet are macroscopically more irregular than at 25°C dry. We again hypothesize that there may be a decrease in flaw sensitivity, but now with increased moisture content rather than temperature. In the epoxy matrix an increase in either temperature or moisture content acts to decrease hydrogen bonding and thus facilitate molecular rearrangement. Furthermore, moisture is known to lower the glass transition temperature of the epoxy [2]. Thus the epoxy's ductility increases and its flaw sensitivity decreases. In addition, residual stresses in the epoxy matrix are reduced. If these effects are of sufficient magnitude, it is reasonable to expect a corresponding decrease in overall composite flaw sensitivity.

There is another difference, on the average, between the morphologies at the two conditions, however. At 25°C wet the filaments protruding from the failure surface tend to be cleaner and longer than at 25°C dry. The micrographs of Figs. 4a and 4c illustrate this difference. This observation is consistent with increased interfacial debonding between filament and matrix. Since the longitudinal tensile strength nonetheless increases, either the increased interfacial debonding does not weaken the overall composite, or any weakening is offset by decreased flaw sensitivity.

The influences of temperature and moisture are combined at 96°C wet. As is shown in Fig. 4d, at this condition the failure morphology contains many bare filaments — filaments that are longer and considerably cleaner than those at 25°C wet. Such long clean filaments are often considered to be filament "pull-outs," but, as is seen in Fig. 5a, there are few corresponding pull-out holes. Figure 5b demonstrates the reason for this discrepancy. The epoxy between filaments has not only debonded but has also broken up and fallen away. We thus conclude that the combined influence of temperature and moisture

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is both to increase interfacial debonding and to make the epoxy more prone to fracture.

Since we have previously assumed that epoxy ductility increases with increased temperature or moisture content, the apparent embrittlement at 96°C wet is contrary to expectations. This result can be explained, however, by a comparison of 25°C wet and 96°C wet testing conditions.

The 96°C wet specimens tested by Clements and Lee actually differed from the 25°C wet specimens in a respect other than temperature. All of their specimens were held at 25°C until shortly before mechanical testing. Adamson [3] has shown that, for temperatures below the conditioning temperature at which moisture was introduced (60°C in this case), the saturation moisture content of graphite/epoxy specimens is inversely proportional to temperature. Thus, as was confirmed by weight-gain studies of Clements and Lee's specimens, their specimens saturated at 60°C picked up yet more water at 25°C. Furthermore, the resulting saturation (or near saturation) moisture content achieved at 25°C is greater than the saturation moisture content at 96°C. Thus, when the temperature of wet specimens held at 25°C was increased, a condition of supersaturation was introduced. Thus, in spite of the essentially 100% humidity of the mechanical test at 96°C wet, desorption would have occurred (and would have continued for several days). During this period of supersaturation, particularly with the aid of the applied tensile stress, covalent bonds may have been broken. Thus, first microcracking and then the type of epoxy cracking shown in Fig. 5b may have resulted.

Three other factors may also have influenced the results at 96°C wet. The glass transition temperature (T_g) of saturated epoxy is altered such that 96°C may have been in or very near the glass transition region of the wet epoxy. This alon if it resulted in a sufficient loss of epoxy strength, might account

for the matrix cracking observed at 96°C wet. In addition, a reduction in T_g might lead to noticeable physical aging of the epoxy even in the brief time (1 to 2 h) Clements and Lee's specimens were held at 96°C. Such physical aging would then produce epoxy embrittlement [4]. Finally, it is also possible that further crosslinking may have occurred in the wet epoxy held at 96°C, again leading to epoxy embrittlement. The importance of these three factors can be neither proven nor disproven without further experiment.

It is unfortunate that the strength data at 96°C wet were unreliable. We would expect the two deleterious effects observed in the failure morphologies to results in a decrease in strength for this condition versus either 25°C wet or 96°C dry. Although the limited strength data reported in Tables 1 and 2 show a decrease in strength, the known end-tab problems render these data questionable. Again further experimentation — with improved end tabs — would be required to define the strength at 96°C wet.

Conclusions

Our conclusions from this study can be summarized as follows:

- Low-energy failure propagation in our specimens probably resulted from undetected specimen defects.
- The damaged edges of our unpolished-edge specimens constituted defects which produced low strengths.
- Regions of altered epoxy in the batch B composite led to lowered strength at elevated temperature or moisture content.
- The failure morphology of postcured specimens showed a tendency toward longer, cleaner filaments and a slightly more brittle matrix than in specimens not postcured. (However, there was no statistical effect of postcuring on strength.)

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- An increase in longitudinal tensile strength with increased temperature may be due to decreased flaw sensitivity.

- Moisture apparently increases strength, perhaps again due to decreased flaw sensitivity, but it also produces more interfacial debonding.

- Combined temperature and moisture produce more interfacial debonding and also apparently allow the epoxy to fracture more easily.

Finally, we would like to emphasize one point. The work of Clements and Lee and this follow-up to that work have shown the considerable effect both quality control and environmental variables can have upon the fiber-dominated property of 0° tensile failure. When several variables are combined — such as "defective" prepreg batch, temperature, and moisture — the degradation in properties may be very severe. Because of these findings, we wish to emphasize the importance of full quality control and environmental characterization of composites prior to use.

Footnotes

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[3]All limits given in this paper are 95% confidence limits, based on the "t" test.

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TABLES 1 -- Summary of 0° tensile strength data of Clements and Lee [1]

Edges	Batch	Tensile strength, MPa			
		25°C		96°C	
		Dry	Wet	Dry	Wet
Unpolished	A	1333 ± 79^a (9)	1366 ± 71 (5)	1418 ± 84 (4)	---
Polished	A	1542 ± 89 (9)	1620 ± 144 (8)	1735 ± 67 (8)	1578 ± 148^b (4)
Polished	B	1540 ± 122 (7)	1443 ± 93 (8)	1500 ± 107 (9)	---

^{a}Limits are 95% confidence limits, based on the "t" test. Numbers in parentheses are numbers of specimens used in statistics.

^{b}These data are questionable. See test for discussion.

TABLE 2 -- Longitudinal tensile strengths of batch A specimens with polished edges after low-energy failure data is eliminated

Edges	Batch	Tensile strength, MPa			
		25°C		96°C	
		Dry	Wet	Dry	Wet
Polished	A	1601 ± 69^a (6)	1765 ± 105 (4)	1730 ± 86 (5)	1593 ± 276^b (3)

^{a}Limits are 95% confidence limits, based on the "t" test. Numbers in parentheses are numbers of specimens used in statistics.

^{b}These data are questionable. See text for discussion.
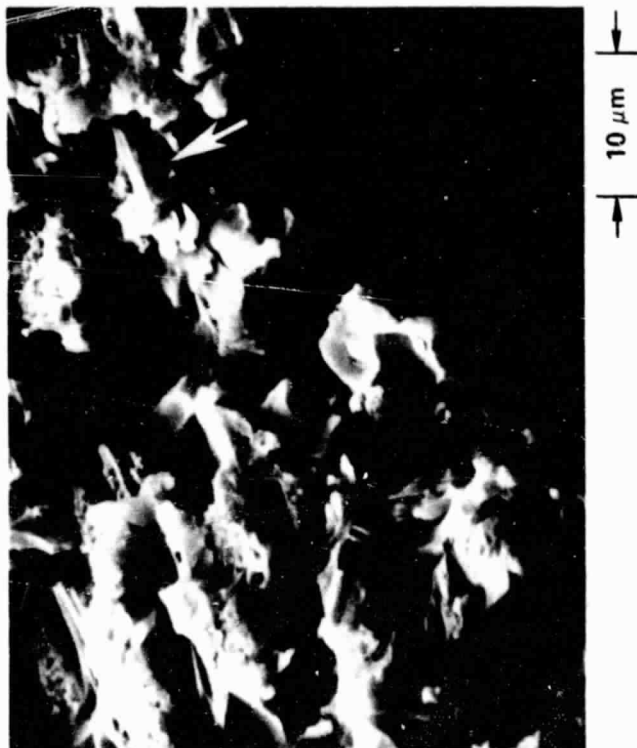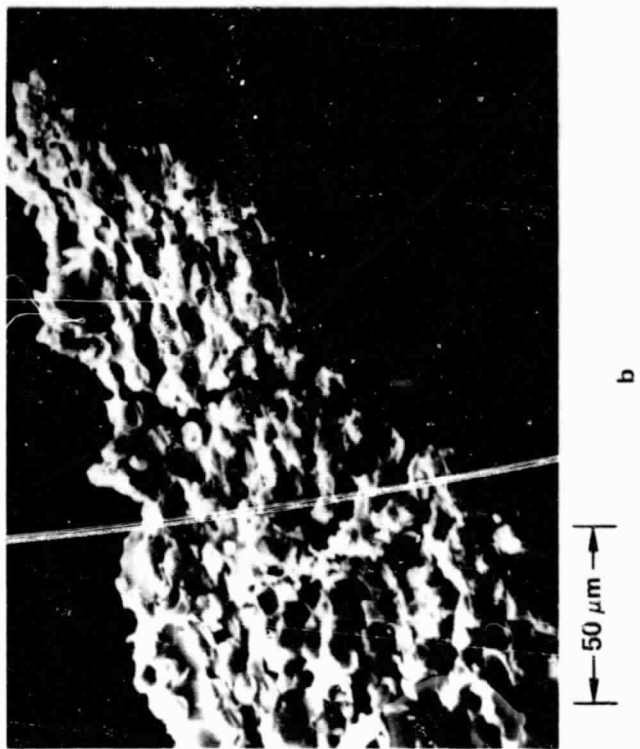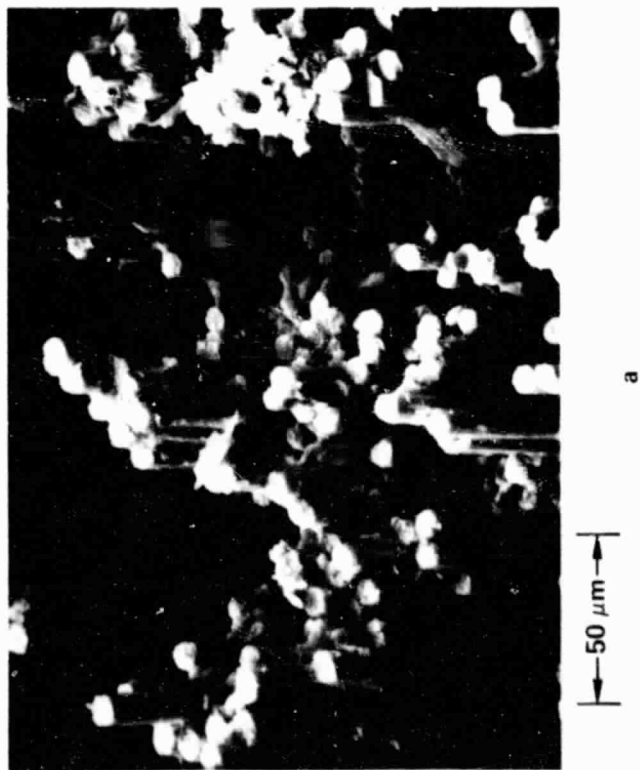
50 μm

b

50 μm

a

10 μm

c

Figure 1.- Scanning electron micrographs comparing failure morphologies resulting from (a) high, and (b) low-energy failure propagation. (c) shows low-energy failure region and "river pattern" (arrow) at higher magnification.
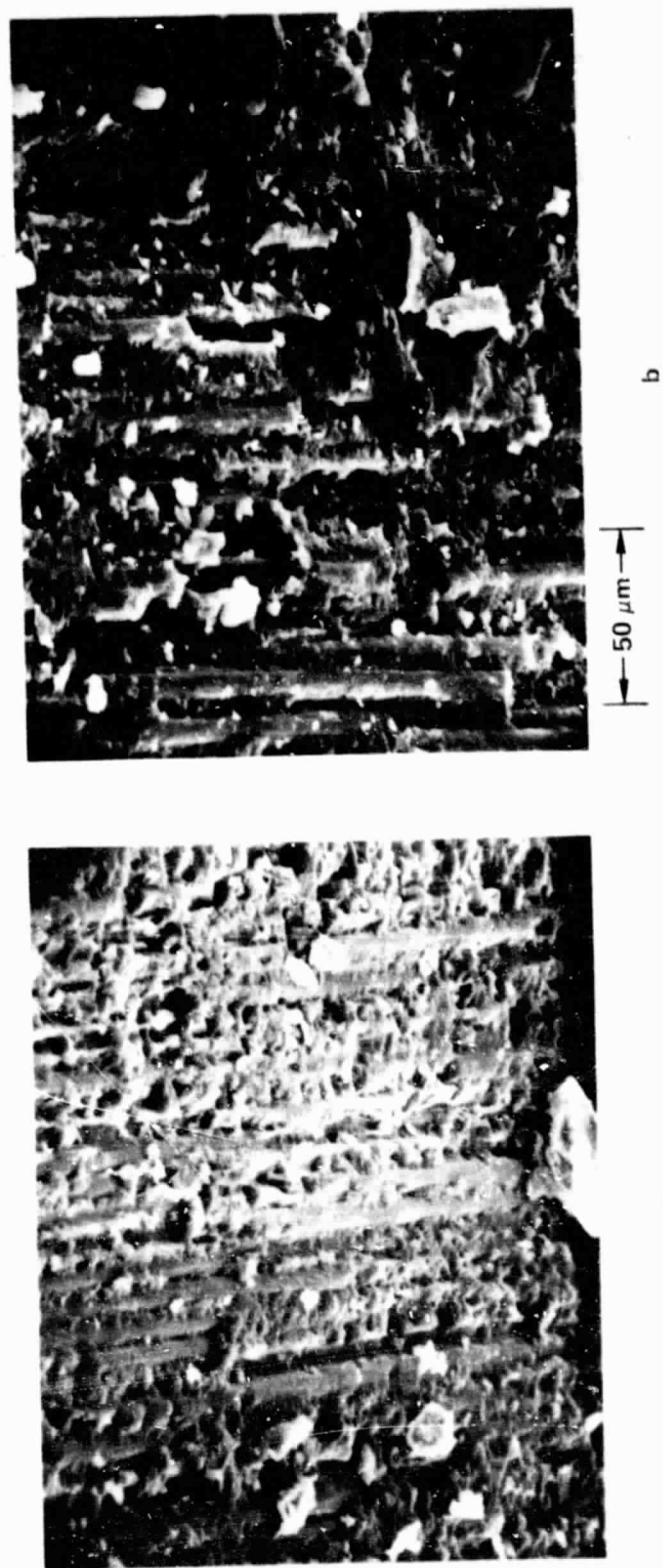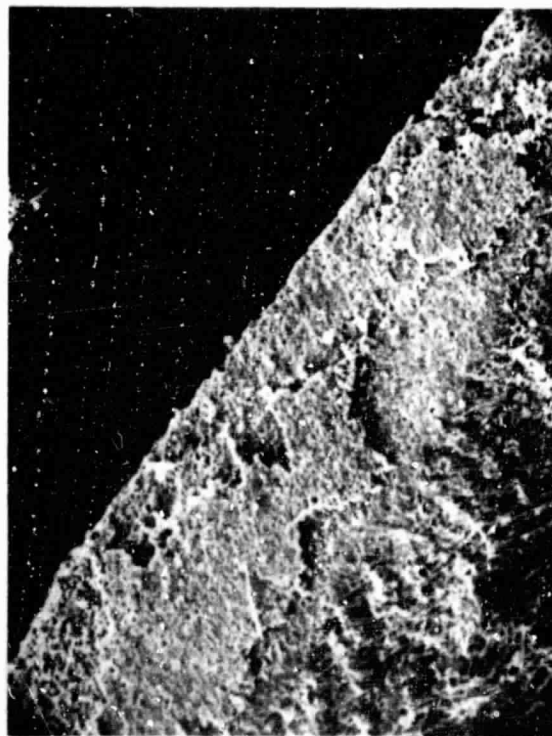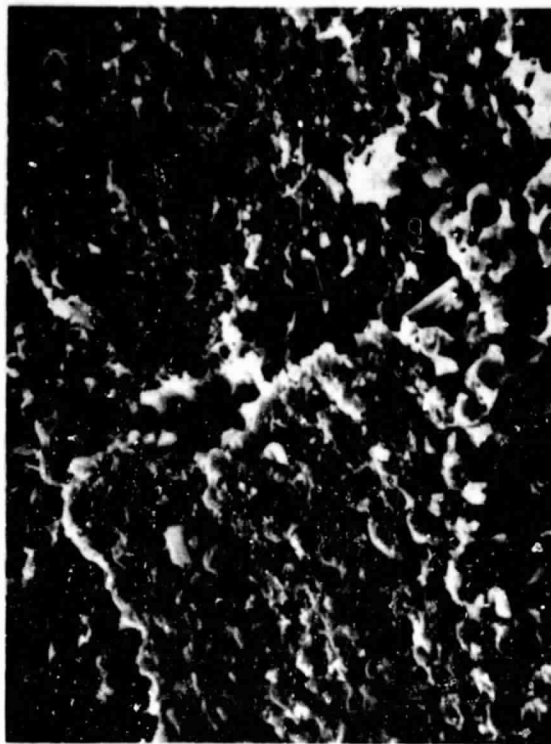
50 μm

Figure 2.- Scanning electron micrographs comparing appearance of (a) unpolished to (b) polished specimen edges.

Figure 3.- Scanning electron micrographs showing at two magnifications a low-energy failure region with obvious differences between different fiber bundles in a batch B speciment (tested at 25°C wet).

Figure 4.- Representative failure morphologies of unpostcured batch A specimens with polished edges tested at four environmental conditions: (a) 25°C dry, (b) 96° dry, (c) 25°C wet, and (d) 96°C wet.
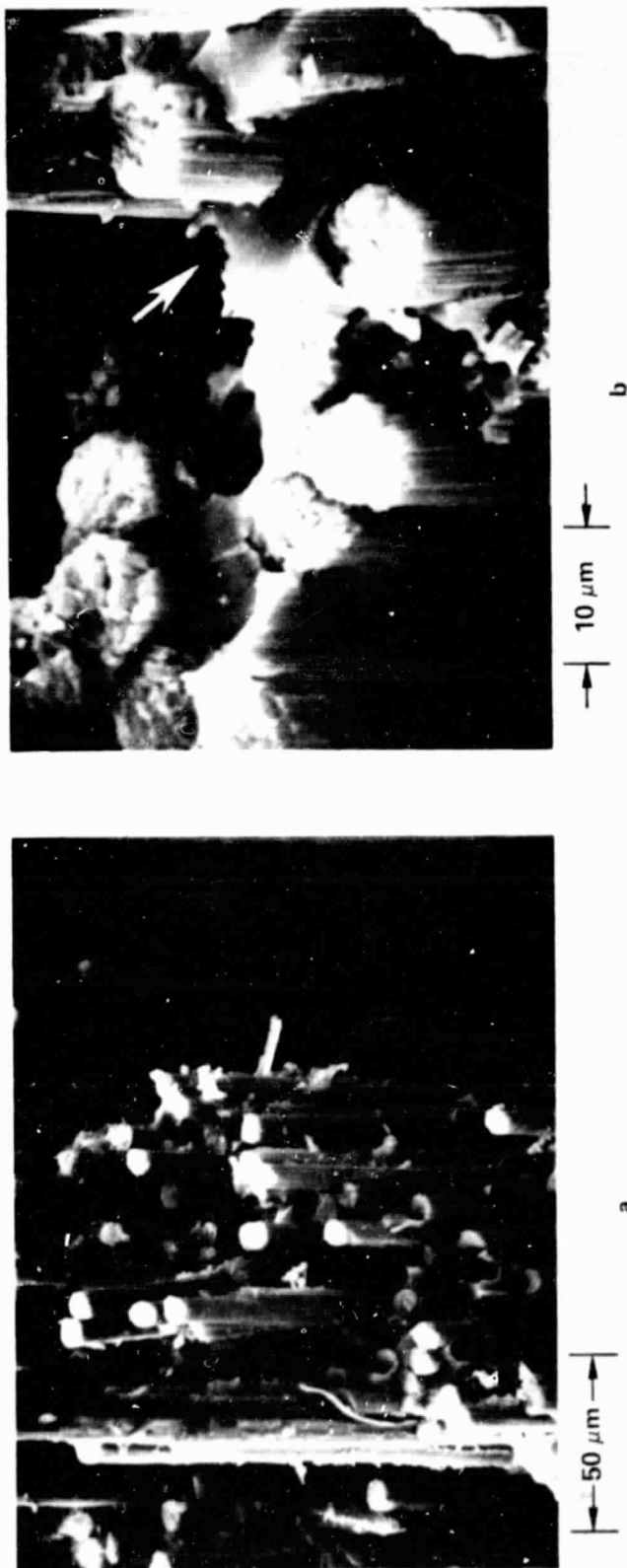
Figure 5.- Scanning electron micrographs of failure surfaces of unpostcured batch A specimens with polished edges tested at 96°C wet. (a) shows long clean filaments but few "pull-out" holes, and (b) shows epoxy that has broken up and is ready to fall away (arrow).